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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/031,208	05/24/2002	Bonnie R. Hames	NREL 98-21	2451

7590

09/11/2003

Paul J White  
National Renewable Energy Laboratory  
1617 Cole Blvd  
Golden, CO 80401

EXAMINER

BARRY, CHESTER T

ART UNIT

PAPER NUMBER

1724

DATE MAILED: 09/11/2003

Please find below and/or attached an Office communication concerning this application or proceeding.

**Office Action Summary**

Application No.

10/031,208

Applicant(s)

HAMES, BONNIE R.

Examiner

Chester T. Barry

Art Unit

1724

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

**Period for Reply**

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If the period for reply specified above is less than thirty (30) days, a reply within the statutory minimum of thirty (30) days will be considered timely.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133).
- Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

**Status**

- 1) ☒ Responsive to communication(s) filed on 16 June 2003.
- 2a) ☐ This action is **FINAL**. 2b) ☒ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

**Disposition of Claims**

- 4) ☒ Claim(s) 1,4-6 and 8 is/are pending in the application.
- 4a) Of the above claim(s) \_\_\_\_\_ is/are withdrawn from consideration.
- 5) ☒ Claim(s) 1,4-6 and 8 is/are allowed.
- 6) ☐ Claim(s) \_\_\_\_\_ is/are rejected.
- 7) ☐ Claim(s) \_\_\_\_\_ is/are objected to.
- 8) ☐ Claim(s) \_\_\_\_\_ are subject to restriction and/or election requirement.

**Application Papers**

- 9) ☒ The specification is objected to by the Examiner.
- 10) ☐ The drawing(s) filed on \_\_\_\_\_ is/are: a) ☐ accepted or b) ☐ objected to by the Examiner.
- Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
- 11) ☐ The proposed drawing correction filed on \_\_\_\_\_ is: a) ☐ approved b) ☐ disapproved by the Examiner.
- If approved, corrected drawings are required in reply to this Office action.
- 12) ☐ The oath or declaration is objected to by the Examiner.

**Priority under 35 U.S.C. §§ 119 and 120**

- 13) ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☐ All b) ☐ Some \* c) ☐ None of:
1. ☐ Certified copies of the priority documents have been received.
  2. ☐ Certified copies of the priority documents have been received in Application No. \_\_\_\_\_.
  3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).
- \* See the attached detailed Office action for a list of the certified copies not received.
- 14) ☐ Acknowledgment is made of a claim for domestic priority under 35 U.S.C. § 119(e) (to a provisional application).
- a) ☐ The translation of the foreign language provisional application has been received.
- 15) ☐ Acknowledgment is made of a claim for domestic priority under 35 U.S.C. §§ 120 and/or 121.

**Attachment(s)**

- 1) ☒ Notice of References Cited (PTO-892)
- 2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
- 3) ☐ Information Disclosure Statement(s) (PTO-1449) Paper No(s) \_\_\_\_\_
- 4) ☐ Interview Summary (PTO-413) Paper No(s). \_\_\_\_\_
- 5) ☐ Notice of Informal Patent Application (PTO-152)
- 6) ☒ Other: COPY OF SPEC. P. 3-6

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Claims 1, 4, 5, 6, 8 are allowed.

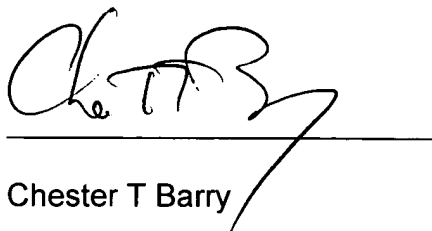
The art cited herein (ref. A – D) describes use of alumina to purify phenol-group bearing substances, such as lignin or phenol, from aqueous media, but the art does not clearly indicate that such phenol-group bearing substances derived from a “biomass hydrolyzate medium,” or suggest or motivate the skilled artisan to select such phenolic compounds be derived from a biomass hydrolyzate medium.

The specification is objected to for minor informalities, such as those indicated by the examiner’s annotations to the enclosed copies of pages 3 – 6. See for example,

<u>Page</u>	<u>Lines</u>
3	4, 5, 7, 13, 14
4	12
5	3, 19
6	9

The examiner regrets not having noted these informalities on the record earlier during prosecution. Correction is required.

Respectfully,



Chester T Barry

703-306-5921

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invention belongs. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, the preferred methods and materials are now described.

As used herein the term Aphenolic@ is an adjective meaning a member of the class of phenols. APhenols@ means the class of aromatic compounds in which one or more hydroxyl groups are attached directly to a benzene ring. Examples of phenols include phenol, cresol and resorcinol. ABiomass-derived phenols@ include the compounds known as guaiacol, syringol, isoeugenol and vanillin.

The process uses a metal oxide, such as titanium dioxide, for the selective adsorption and removal of phenolic compounds from an aqueous solution, such as a biomass-hydrolyzate medium. Dissolved sugars in the solution are thereby concentrated. Adsorption is highly selective, and provides an efficient method for the fractionation of a biomass-hydrolyzate, 90% of the hydrolyzate=s dissolved lignin being removed without a measurable decrease in the solution=s dissolved sugar concentration. Selectivity is attributable to the metal oxide=s preferential binding with those oxygen molecules which are located on adjacent (ortho) carbons of the aromatic ring structures.

With reference now to Figure 1, the starting material is a biomass hydrolysis liquor 1. The hydrolysis liquor 1 is mixed in contacting step 4, as a suspension, with a metal oxide 2, such as a Norton Chemical Process Products Corporation, Akron, Ohio high-surface-area  $\text{TiO}_2$  1/8 " extrudate type XT25384. High separation efficiency is generally achieved by using an amount or weight (wt) of  $\text{TiO}_2$ , which is twice the estimated phenol content of the liquor. This ratio varies, however, with the form, source, active surface area, and liquid-contact surface area of the  $\text{TiO}_2$ , to be used. Separation efficiency also varies with the age of the aqueous mixture and source of the biomass. Producing hydrolyzate under conditions of high severity also reduces the separation efficiency.

Selective adsorpting step 6 is accomplished using all grades of  $\text{TiO}_2$ . The rate and efficiency of the adsorption of aromatic compounds with  $\text{TiO}_2$  is dependent upon the  $\text{TiO}_2$  active surface area. Anatase titanium dioxide, preferred to the rutile form, may be used.

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surface-area formulation, including powders, thin-films, sol-gel crystals, and extruded pellets. Vanadium oxide and zirconium oxide, and at pH in a range of greater than 7.0 manganese dioxide, silica, and alumina, may also be used.

Depending upon the quantity of the aromatic compounds to be removed, a batch reaction vessel or plug flow reactor may be used as an adsorption vessel. In a batch reactor, the retention time is preferably 30 minutes. In a plug flow column, the retention time is preferably 15 minutes. These retention times typically result in a separation of up to 90-weight % of the aromatics from the hydrolyzate 1. Longer retention times are desirable where the separation is carried out at a low pH. For example, the adsorption is slower in the pH range of 2 - 6 and occurs more rapidly when the pH is in the range of 7 -10.

The process retains its efficiency and selectivity throughout a temperature in the range of 20°C-90°C. Performing the selective adsorption under conditions of elevated temperature and pH does not affect adsorption selectivity relative to the carbohydrate fraction.

However, above pH 6, some carbohydrate degradation products, such as 5-(hydroxymethyl) furfural and furfural, are also adsorbed on the metal oxide surface. At combinations of higher pH and temperature some entrainment of soluble salts occurs on the metal oxide surface when the hydrolyzate 1 and metal oxide 2 mixture contains salts having a lower solubility at higher temperatures, such as calcium sulfate. Raising both the temperature and the pH does not affect the adsorption selectivity of this process for lignin. After contacting the hydrolyzate and metal oxide, adsorption preferably includes agitating the mixture for a time sufficient to allow the colloidal particles to deposit on the TiO<sub>2</sub> particulate surfaces, as indicated by a clearing of the suspension, and allowing the suspension to settle at room temperature for 1 hour. The adsorbed complex is then separated in separation step 8. Separation may be accomplished using a glass-fiber filter. The carbohydrate fraction of the hydrolysis liquor is contained in the sugars filtrate 10.

A unique aspect of the invention is its high separation selectivity for lignin in an aqueous hydrolysis liquor having an excess of monomer sugars. More than 90% of the solubilized lignin can be removed from the hydrolyzate without any loss of glucose or xylose. When using TiO<sub>2</sub>

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extruded pellets as an adsorbent, a slight concentration effect is observed during the adsorption process. This effect may be due to hydration of the metal oxide and the exclusion of sugars from the metal oxide=s surface. Solid state nuclear magnetic resonance analysis of lignin model compounds, adsorbed on the  $\text{TiO}_2$  surface, has suggested that the lignin selectivity is due, at least in part, to an affinity of titanium for adjacent oxygen molecules which are located on the aromatic ring structure of the adsorbed substrates. It has been found that, through chemical shifts in  $^{13}\text{C}$  nmr between lignin model compounds both before and after complexation with titanium alkoxides, these molecules bind preferentially through the phenolic oxygen and the oxygen of the adjacent methoxyl group. The biomass-derived aromatic substituents have two main substitution patterns, commonly known as guaiacyl and syringyl, which contain the functional groups necessary for the selective fractionation. Although titanium, and many other transition metals, are known to be highly oxyphilic, the affinity of this functionality for these metal oxides is so strong that in the presence of these aromatic compounds, even highly oxygenated carbohydrate-derived compounds are excluded from the metal oxide surface.

The process may also include a regeneration step 14. In this step, the  $\text{TiO}_2$  adsorbents are easily regenerated using combustion of the complex at  $400^\circ\text{C}$  for 15 minutes. An estimated 100-500 regeneration cycles may be utilized without a significant reduction in adsorption capacity or selectivity. It is preferred to regenerate the  $\text{TiO}_2$  at a temperature of less than  $600^\circ\text{C}$  in order to avoid an anatase to rutile form conversion, which decreases the metal oxide=s capacity for adsorption. A simple regeneration wash step using dilute sulfuric acid may also be used to increase the lifetime of  $\text{TiO}_2$  adsorbents when the contacting step 4 is carried out at a high pH. When using a pH greater than 7, an additional step of acid washing the adsorbent is desirable. Regeneration of a manganese dioxide adsorbent has also been demonstrated at  $575^\circ\text{C}$  for 15 minutes.

### EXAMPLE

This example illustrates the process of removing phenolic compounds from an aqueous biomass hydrolysis liquor using  $\text{TiO}_2$  as the metal oxide. The hydrolysis liquor was an acid

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hydrolyzate of hybrid yellow poplar. In this example the following three samples were prepared.

Sample No. 1 was prepared by mixing a 50 ml aliquot, of a well mixed hydrolysis liquor containing a larger amount of suspended solids, in contact with 10 grams of Norton high-surface-area  $\text{TiO}_2$ , in a 100 ml beaker. The sample was agitated by hand for approximately 5 minutes. until the mixture became clear (colloidal particulates deposited on the surface of the  $\text{TiO}_2$ ). The mixture was allowed to settle at room temperature for 1 hour. The  $\text{TiO}_2$  mixture was filtered through a glass Watman GFC filter and the filtrate was stored in a glass container.

Samples Nos. 2 and 3 were prepared by mixing a 50 ml aliquot, of a well-mixed hydrolysis liquor again containing a large amount of suspended solids, in contact with 10 grams of high surface area  $\text{TiO}_2$  in a 100 ml beaker. Unlike sample No. 1, the  $\text{TiO}_2$  in sample No. 2 was left in solution without stirring at room temperature for 8 hours (sample No. 2) prior to the removal of the  $\text{TiO}_2$  phenolic-adsorption-complex, by gravity filtration. Half of the liquid (20 ml) was decanted and filtered for analysis, and the other half of the solution was retained in contact with the  $\text{TiO}_2$  overnight (sample No. 3). The beaker was covered with aluminum foil to minimize evaporation. After 20 hours, the remaining liquid of sample No. 3, was decanted from the  $\text{TiO}_2$  complex and filtered through a Watman GFC glass filter. The filtrates for each sample were diluted in dilute  $\text{H}_2\text{SO}_4$  and analyzed for their phenol concentrations by measuring UV absorbency at 204 nm. In addition, the glucose concentration of the filtrate was measured for each sample using a Yellow Springs Instruments glucose analyzer.

The results of this example are summarized in Table 1. In the table, most of the adsorption occurs within the first hour and very little change is observed in either adsorption or selectivity with prolonged exposure. The absorbance at 204 nm (measured using a ultra-violet/visible spectrometer) reflects the concentration of the phenolic compounds remaining in the treated liquor. The absorbance at 282 nm reflects the concentration of furfural and 5-(hydroxymethyl) furfural. The dilution factor (D) was the dilution used to bring the solution to a concentration where the absorbency is proportional to the concentration.